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(54) Preparation of Polyesters from  
Diels Alder Adducts

(57) Ester-containing polyols are prepared by reaction in a first stage of a hexahalocyclopentadiene with maleic anhydride in a mole ratio of hexahalocyclopentadiene to maleic anhydride in excess of 1:1. The resulting product is a 1,4,5,6,7,7-hexahalobicyclo[2.2.1]-5-heptene-

2,3-dicarboxylic acid anhydride mixed with excess hexahalocyclopentadiene. An organic compound having at least two active hydrogen atoms and an alkylene oxide may then be added to the mixture with heating to cause the anhydride product of the first reaction to react with the organic compound and the alkylene oxide, producing an ester-containing polyol which is particularly useful in the preparation of flame-retardant polyurethane foams.

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## SPECIFICATION

## Preparation of Ester-containing Polyols and Intermediates Therefor

This invention relates to a new method of preparing ester-containing polyols via chlorendic anhydride or a related compound, which is prepared in the same reactor as that in which a subsequent reaction of it with an organic compound having at least two active hydrogens and an alkylene oxide is to be performed.

It has become increasingly important to impart flame-resistant properties to polyurethane plastics. This is particularly true where cellular polyurethanes are used, for example, as insulation, and to prevent the risk of fire in the daily use of other items. Numerous methods are known for imparting flame-resistant properties to polyurethane plastics such as through the use of halogenated compounds. Such halogenated compounds include novel ester-containing polyols having halogen atoms chemically bound therein and having relatively low viscosity. Such ester-containing polyols have been prepared in the prior art through the use of three essential reactants, namely: (1) organic compounds having at least two active hydrogen atoms, (2) halogen-containing organic acid anhydrides, particularly the 1,4,5,6,7,7-hexahalobicyclo[2.2.1]-5-heptene-2,3-dicarboxylic acid anhydrides, and (3) alkylene oxides. The compound wherein the halogen is chlorine is generally preferred and is well known as chlorendic anhydride. The expression, "chlorendic anhydride and related compounds" used in this specification means the 1,4,5,6,7,7-hexahalobicyclo[2.2.1]-5-heptene-2,3-dicarboxylic acid anhydrides. In the prior art, these halogenated polycarboxylic acid anhydrides are prepared by reacting hexahalocyclopentadiene with maleic anhydride, the mole ratio of the diene to the anhydride generally being 1:1 or less. While ester-containing polyols prepared from chlorendic anhydride and related compounds impart excellent low-smoke and low-flame-spread properties to rigid polyurethane foams made therefrom, they are expensive and in short supply. Moreover, the handling of the chlorendic anhydride and related compounds in large quantities in manufacturing operations is time-consuming because the commercial material tends to cake. In addition, the dust from the material presents toxicity problems. Also, when employing commercial chlorendic anhydride and related compounds for the production of ester-containing polyols, it is generally necessary to use liquid polyols to dissolve the anhydride which is normally sold in solid form.

Accordingly, this invention seeks to provide an improved process for preparing chlorendic anhydride and related compounds and ester-containing polyols therefrom which overcomes or reduces the above disadvantages of the prior art processes.

It is known from U.S. Patents 3,585,185 and 4,144,395 to prepare ester-containing polyols by the reaction of an alkylene oxide, an organic compound having at least two active hydrogen atoms, and an acid anhydride such as chlorendic acid anhydride. U.S. Patent 2,779,700 discloses the Diels-Alder reaction of a hexahalocyclopentadiene such as hexachlorocyclopentadiene and an unsaturated polycarboxylic acid anhydride such as maleic anhydride to produce chlorendic anhydride and related compounds. U.S. Patent 2,752,361 teaches the reaction of hexachlorocyclopentadiene with alpha-substituted alkylenic succinic acids or anhydrides as represented by itaconic acid and aconitic acid. Example 1 of that patent teaches the use of 3.3 moles of hexachlorocyclopentadiene with 3 moles of itaconic anhydride. However, the reaction is actually a nonanalogous reaction and the reaction product is substantially different from the chlorendic anhydride and related compounds produced by the method of this invention.

According to the present invention there is provided a process for preparing an ester-containing polyol comprising reacting a hexahalocyclopentadiene with maleic anhydride in a mole ratio of diene to anhydride in excess of 1:1 to produce 1,4,5,6,7,7-hexahalobicyclo[2.2.1]-5-heptene-2,3-dicarboxylic acid anhydride mixed with excess hexahalocyclopentadiene, and adding an organic compound having at least two active hydrogen atoms and an alkylene oxide to the mixture with heating to cause the 1,4,5,6,7,7-hexahalobicyclo[2.2.1]-5-heptene-2,3-dicarboxylic acid anhydride to react with the organic compound and the alkylene oxide to produce the polyol.

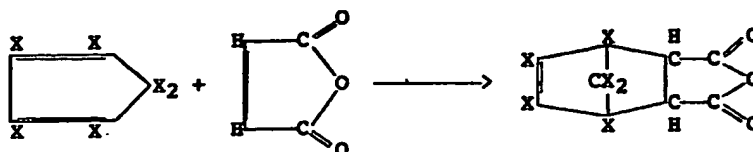
The 1,4,5,6,7,7-hexahalobicyclo[2.2.1]-5-heptene-2,3-dicarboxylic acid anhydride is prepared in the reactor in which it is to be used for further reaction, by addition of a hexahalocyclopentadiene, a high-boiling liquid, to maleic anhydride, suitably at 130 to 180°C, preferably 150—160°C, the reaction suitably being continued for 6 to 10 hours, preferably 8 to 10 hours. An excess of the diene (preferably 0.5 mole excess) is employed so that the high-melting product, having a melting point of 271°C in the case of chlorendic anhydride, is dissolved and/or slurried in it whereby the organic compound having at least two active hydrogen atoms and alkylene oxide can be added at a temperature of from 50 to 150°C. When the ester-containing polyol preparation is completed, which may be determined by monitoring the acid number until a low acid number is attained, processing can be carried out in the usual manner with the exception that the excess diene can be recovered, for example by stripping, and can be reused for preparing the next batch.

The present invention avoids the tedious charging and toxicity problems of the prior art by preparing the anhydride in the same reactor in which the ester-containing polyol will be prepared; and by using a more easily manipulated maleic anhydride which is available in briquette or molten form to react with the liquid hexahalocyclopentadiene. A further advantage of the present invention is the

possibility of using high-melting solid initiators for preparing the ester-containing polyol since the chlorendic anhydride or related compound is slurried in the excess diene whereas, in the normal procedure, a solid chlorendic anhydride or related compound would have to be added to a liquid polyol and therefore a solid initiator could not be employed. In addition to the economies of recycling the recovered high-boiling diene to the next batch, pollution is also avoided through such recycling.

Another advantage of the present invention is that raw material costs for the chlorendic anhydride and related compounds is lowered by avoiding purification and isolation thereof. Since the anhydride is left in the reactor for preparation of the ester-containing polyol, this process results in substantial reduction in the cost of the chlorendic anhydride employed to prepare the ester-containing polyol.

The preferred anhydride for use in accordance with this invention is chlorendic anhydride. Others that can be prepared using the corresponding hexahalocyclopentadiene include 1,4,5,6,7,7-hexabromobicyclo[2.2.1]-5-heptene-2,3-dicarboxylic acid anhydride and 1,4,5,6-tetrachloro-7,7-difluorobicyclo[2.2.1]-5-heptene-2,3-dicarboxylic acid anhydride. In addition, other acid anhydrides having the structure of chlorendic acid anhydride except for substitution of the chlorine atoms in whole or in part by bromine, iodine, and fluorine atoms may be prepared from the corresponding hexahalocyclopentadiene. The reaction of the diene with maleic anhydride is as set forth below.



In the above equation, X represents a halogen, i.e., chlorine, bromine, iodine or fluorine.

Organic compounds having at least two active hydrogen atoms which may be employed in the preparation of the ester-containing polyols according to the present invention are well known in the art. Examples of such organic compounds include polyhydric alcohols such as ethylene glycol, propylene glycol, the isomeric n-butylene glycols, 1,5-pentane diol, 1,6-hexane diol, glycerol, trimethylolpropane, 1,2,6-hexane triol, sorbitol, sucrose, alpha-methyl glucoside, pentaerythritol; and alkylene oxide condensates of compounds having at least two active hydrogen atoms which are well known in the art as evidenced by U.S. Patents Nos. 1,922,459; 3,190,927, and 3,346,557. They are generally prepared by the catalytic condensation of an alkylene oxide or mixture of alkylene oxides either simultaneously or sequentially with a compound having at least two active hydrogen atoms. Representative compounds include the polyhydric alcohols listed above; acids such as inorganic polyhydric acids, e.g. phosphoric, phosphorous, boric, and organic acids such as adipic acid, succinic acid, aconitic acid, and trimellitic acid; amines such as methylamine, ethylamine, ethylenediamine, diethylene-triamine, toluenediamine, aniline, methylenedianiline, piperazine, and trisopropanolamine; phenolic compounds such as bisphenol, pyrogallol, resorcinol, inositol; mercaptans such as 1,2-ethanedithiol and 1,2,3-propanedithiol; and acid amides such as acetamide and benzene sulfonamide. Mixtures of any of the above may also be employed. Generally, the condensates useful in the present invention will have a molecular weight between 100 and 10,000, preferably between 300 and 6,000. Any of the alkylene oxides listed below may be employed in the preparation of these condensates.

Alkylene oxides which may be employed in the preparation of the ester-containing polyols as the alkylene oxide reactant and in the preparation of the above condensate include ethylene oxide, propylene oxide, the isomeric normal butylene oxides, hexylene oxide, octylene oxide, dodecene oxide, methoxy and other alkoxy propylene oxides, glycidyl ethers or esters, styrene oxide, and cyclohexene oxide. Halogenated alkylene oxides may also be used, such as epichlorohydrin, epiodohydrin, epibromohydrin, 3,3-dichloro-propylene oxide, 3-chloro-1,2-epoxypropane, 3-chloro-1,2-epoxybutane, 1-chloro-2,3-epoxybutane, 3,4-dichloro-1,2-epoxybutane, 1,4-dichloro-2,3-epoxybutane, 1-chloro-2,3-epoxybutane, and 3,3,3-trichloropropylene oxide. Mixtures of any of the above alkylene oxides may also be employed.

The ester-containing polyols are generally prepared by heating the three reactants at temperatures from about 50°C to 150°C, preferably about 80°C to 140°C, for about 0.5 to 10 hours, preferably about 6 to 8 hours. Temperatures below 150°C must be maintained to prevent the reaction of carboxy and hydroxy groups with the formation of water. The reaction is generally carried out under a pressure of from 0 to about 100 p.s.i.g. and preferably about 30 to 90 p.s.i.g. Alternatively, the organic compound having at least 2 active hydrogen atoms is added to the anhydride-diene mixture in the reaction vessel and heated to about 50°C to 150°C for zero to about five hours. Thereafter, the alkylene oxide is added to the reaction mixture under pressure of about 30 to 90 p.s.i.g. while maintaining a reaction temperature of from about 75°C to 150°C. Completion of the reaction requires about 3 to 6 hours. The reaction mixture may be filtered and stripped of volatiles by heating for about one-half hour to three hours at about 130°C to 150°C under less than about 10 millimeters of

mercury. The excess hexahalocyclopentadiene obtained by stripping may be reused in the preparation of more chlorendic anhydride and related compounds.

The amounts of reactants employed in the preparation of the ester-containing polyols may vary. Generally, however, a mole ratio of organic compound having at least two active hydrogen atoms to chlorendic anhydride or related compounds of from about 1:01 to 1:12, preferably from about 1:1 to 1:6, will be employed. The amount of alkylene oxide employed will be such to reduce the acid number of said organic compound-anhydride reaction mixture to about five or less, preferably about one or less. The hydroxyl number of the ester-containing polyol will vary considerably. Generally, however, the polyols will have a hydroxyl number of from about 20 to 600, preferably from about 35 to 500.

In a preferred embodiment of the present invention, the foregoing ester-containing polyols are employed in the preparation of polyurethane compositions, particularly polyurethane foams. The resulting polyurethane products exhibit marked improvements in flame-retardant properties without impairment of the other physical properties of the products. Moreover, the lower viscosity of these polyols enables them to be useful in the preparation of sprayable polyurethane compositions. The polyurethane products are generally prepared by the reaction of the ester-containing polyol with an organic polyisocyanate, optionally in the presence of additional polyhydroxyl-containing components, chain-extending agents, catalysts, surface-active agents, stabilizers, blowing agents, fillers, and pigments. Suitable processes for the preparation of cellular polyurethane plastics are disclosed in U.S. Reissue Patent 24,514 together with suitable machinery to be used in conjunction therewith.

In addition to being useful in the preparation of polyurethanes, the ester-containing polyols prepared from the chlorendic anhydride and related compounds, in accordance with this invention, find utility as precursors in the preparation of graft copolymer dispersions as discussed in U.S. Patent No. 3,652,639 and U.S. Reissue Patent No. 29,014.

The following examples illustrate the invention. All parts and percentages are by weight.

#### Example 1

To a 1-liter, 4-necked round bottom flask, equipped with stirrer, thermowell, and condenser, was charged 98 grams (1.0 mole) maleic anhydride and 100 grams (0.37 mole) hexachlorocyclopentadiene. The charge was heated to 115°C under a nitrogen sweep, and 175.7 grams (0.64 mole) of hexachlorocyclopentadiene was added dropwise from a side-armed addition funnel, allowing the exotherm reaction to increase the temperature to 150—160°C.

The addition required 2 hours, after which the reaction mixture was stirred at 150—160°C for an additional 8 hours. During this reaction period, an additional 134 grams (0.49 mole) of hexachlorocyclopentadiene was added in several increments to keep the flask contents fluid. The reaction mixture was then cooled to 110°C and 92 grams (1.0 mole) of glycerin added. The mixture was heated to 121°C and 131 grams (2.25 moles) of propylene oxide was added, over 2.5 hours, allowing the temperature to rise to 130—145°C where it was maintained during the rest of the addition. The reaction mixture was stripped at 125—127°C and <1 millimeter Hg. for 1 hour.

The amber-colored product had a hydroxyl number of 296; an acid number of 0.167; a water content of 0.02 percent; a chlorine content of 37.9 percent and a Brookfield viscosity at 25°C of >8,000,000 cps.

Dilution of the product with a propylene oxide adduct of glycerine having a molecular weight of 310 to 85 percent by weight gave a material having a viscosity of 1,380,000 cps. at 27°C.

#### Example 2

To an apparatus identical to that of Example 1 was charged 98 grams (1.0 mole) maleic anhydride and 100 milliliters (approximately 0.5 mole) of hexachlorocyclopentadiene. The charge was heated to 140°C and 273 grams (1.0 mole) of the diene was added at 137—150°C over one hour. The fluid reaction mixture was stirred at 133—157°C for 10.5 hours, cooled to 135°C and a mixture of 92 grams (1.0 mole) glycerine and 100.5 grams (0.324 mole) of a propylene oxide adduct of a glycerine having a molecular weight of 310 was added. 145 grams (2.5 moles) propylene oxide was then added at 130—144°C over a 0.6 hour period. The mixture was then stirred at reflux (134—140°C) for 4.5 hours when the acid number was 0.15. The product was stripped two hours at 130°C and 0.5 hour at 152°C and 2—3 millimeters Hg.

Analysis gave a hydroxyl number of 314; an acid number of 0.313; a water content of 0.01 percent; a chlorine content of 32 percent; and a Brookfield viscosity at 26°C of 2,600,000 cps.

#### Example 3

The strippings from Example 2 were charged (after evaporation at reduced pressure to remove propylene oxide) to a reactor, equipped as above, along with 98 grams (1.0 mole) of maleic anhydride. The flask contents were heated to 135°C and 273 grams (1.0 mole) hexachlorocyclopentadiene was added over 1.25 hours at 135—150°C. The reaction mixture was stirred at 150—156°C for eight hours, cooled to 135°C and a mixture of 92 grams (1.0 mole) glycerin and 100.5 grams (0.324 mole) of a propylene oxide adduct of glycerine having a molecular weight of 310 was added. Propylene oxide, 131 grams, (2.5 moles) was then added at 126—149°C over 0.75 hour and the reaction mixture

stirred at reflux at 132—136°C for four hours. After three hours, the acid number was 0.13. The product was stripped (1.75 hours at 145—150°C, 3 millimeters Hg) and analysis gave a hydroxyl number of 314; an acid number of 0.49; a water content of 0.07 percent; a chlorine content of 32.4 percent; and a viscosity of 2,028,000 cps. at 25°C.

#### 5 Example 4

The strippings from Example 3 were charged to a similar set up and the same quantities of maleic anhydride, hexachlorocyclopentadiene, glycerin, propylene oxide adduct of glycerine having a molecular weight of 310 and propylene oxide and the same temperatures were employed as in Example 3. The stripped product had a hydroxyl number of 322; an acid number of 0.16; a water content of 0.04 percent; a chlorine content of 30.4 percent; and a viscosity of 2,200,000 cps. at 24°C.

A summary of the properties of Examples 2, 3 and 4, representing an initial run and 2 recycles, and indicating the degree of reproducibility, are as follows:

| Example                          | 2            | 3            | 4            |
|----------------------------------|--------------|--------------|--------------|
| Hydroxyl number                  | 314          | 314          | 322          |
| Acid number                      | 0.313        | 0.49         | 0.16         |
| Water content, %                 | 0.001        | 0.14         | 0.14         |
| Chlorine content, %              | 32.0         | 32.4         | 30.4         |
| Brookfield viscosity<br>cps./°C. | 2,600,000/26 | 2,030,000/25 | 2,200,000/24 |

#### 20 Claims

1. A process for the preparation of an ester-containing polyol comprising reacting a hexahalocyclopentadiene with maleic anhydride in a mole ratio of hexahalocyclopentadiene to maleic anhydride in excess of 1:1 to produce 1,4,5,6,7,7-hexahalobicyclo[2.2.1]-5-heptene-2,3-dicarboxylic acid anhydride mixed with excess hexahalocyclopentadiene, and adding an organic compound having at least two active hydrogen atoms and an alkylene oxide to the mixture with heating to cause the 1,4,5,6,7,7-hexahalobicyclo[2.2.1]-5-heptene-2,3-dicarboxylic acid anhydride to react with the organic compound and the alkylene oxide.

2. A process as claimed in claim 1 wherein the hexahalocyclopentadiene is hexachlorocyclopentadiene and the anhydride produced in the first step is chlorendic anhydride.

3. A process as claimed in claim 1 or 2 wherein the temperature for the reaction of the diene with maleic anhydride is from 130 to 180°C and the temperature for the reaction of the anhydride product with the organic compound and the alkylene oxide is from 50 to 150°C.

4. A process as claimed in any of claims 1 to 3 wherein the excess hexahalocyclopentadiene is removed from the ester-containing polyol reaction product and recycled for the preparation of the anhydride.

5. A process as claimed in claim 4 wherein the volatiles are stripped from the polyol reaction product for 0.5 to 3 hours at 130 to 150°C and a pressure of less than 10 millimeters of mercury.

6. A process as claimed in any of claims 1 to 5 wherein the reaction of the diene with maleic anhydride is carried out for 6 to 10 hours and the reaction of the anhydride product with the organic compound and the alkylene oxide is carried out for 0.5 to 10 hours at a pressure of 0 to 100 p.s.i.g.

7. A process as claimed in any of claims 1 to 6 wherein the organic compound is added to the anhydride product followed by heating to 50 to 150°C for 0 to 5 hours after which the alkylene oxide is added under pressure of 30 to 90 p.s.i.g. and the temperature maintained at 75 to 150°C for 3 to 6 additional hours.

8. A process for the preparation of an ester-containing polyol carried out substantially as described in any of the foregoing Examples.

9. A process for the preparation of 1,4,5,6,7,7-hexahalobicyclo[2.2.1]-5-heptene-2,3-dicarboxylic acid anhydride which comprises reacting a hexahalocyclopentadiene with maleic anhydride at a mole ratio of hexahalocyclopentadiene to maleic anhydride of greater than 1:1.

10. A process as claimed in claim 9 wherein the hexahalocyclopentadiene is hexachlorocyclopentadiene and chlorendic anhydride is produced.

11. A process as claimed in claim 9 or 10 wherein the reaction is carried out for 6 to 10 hours at a reaction temperature of 130 to 180°C.

12. A process as claimed in any of claims 9 to 11 wherein the amount of hexahalocyclopentadiene is sufficiently in excess to dissolve the product of the reaction.

13. A process as claimed in claim 12 wherein the amount of hexachlorocyclopentadiene is approximately 0.5 mole in excess of a 1:1 mole ratio.

14. An ester-containing polyol when prepared by a process as claimed in any of claims 1 to 8.

5 15. Flame-retardant polyurethane foams when prepared from an ester-containing polyol as claimed in claim 1 and a polyisocyanate. 5

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